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Intrinsic point defects in inorganic perovskite CsPbI₃ from first-principles prediction

Yifan Li,¹ Chenhui Zhang,² Xixiang Zhang,² Dan Huang,³ Qian Shen,¹ Yingchun Cheng,^{1,a)} and Wei Huang¹

¹Key Laboratory of Flexible Electronics (KLOFE) and Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211816, China

²Physical Science and Engineering Division (PSE), King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia

³Guangxi Key Laboratory for Relativistic Astrophysics, Guangxi Colleges and Universities Key Laboratory of Novel Energy Materials and Related Technology, Guangxi Novel Battery Materials Research Center of Engineering Technology, School of Physical Science and Technology, Guangxi University, Nanning 530004, China

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Cubic inorganic perovskite CsPbI₃ is a direct bandgap semiconductor, which is promising for optoelectronic applications, such as solar cells, light emitting diodes, and lasers. The intrinsic defects in semiconductors play crucial roles in determining carrier conductivity, the efficiency of carrier recombination, and so on. However, the thermodynamic stability and intrinsic defect physics are still unclear for cubic CsPbI₃. By using the first-principles calculations, we study the thermodynamic process and find out that the window for CsPbI₃ growth is quite narrow and the concentration of Cs is important for cubic CsPbI₃ growth. Under Pb-rich conditions, V_{Pb} and V_{I} can pin the Fermi energy in the middle of the bandgap, which results in a low carrier concentration. Under Pb-poor conditions, V_{Pb} is the dominant defect and the material has a high concentration of hole carriers with a long lifetime. Our present work gives an insight view of the defect physics of cubic CsPbI₃ and will be beneficial for optoelectronic applications based on cubic CsPbI₃ and other analogous inorganic perovskites. Published by AIP Publishing. <https://doi.org/10.1063/1.5001535>

In the past few years, hybrid organic-inorganic halide perovskites with the formulation of ABX₃ (A is an organic cation, B is Pb or Sn, and X is a halogen) have attracted enormous attention for solar cell applications.^{1–4} The most widely studied hybrid organic-inorganic perovskite materials are formamidinium lead triiodide (NH₂CHNH₂PbI₃) and methylammonium lead triiodide (CH₃NH₃PbI₃).^{5,6} Perovskite materials are regarded as the most competitive candidates because of their low cost and high power conversion efficiencies (over 20%).^{7–9} Moreover, the materials are also promising samples for light emitting diodes, lasers, and photodetectors.^{10–12} However, the application of hybrid ABX₃ is restricted by environmental degradation caused by heat and humidity.^{13–16} To overcome these issues, all-inorganic halide perovskite materials have been considered as alternatives.^{17–20} Among these materials, cubic CsPbI₃ is a promising candidate for optoelectronic properties,^{15,17,21} because of its direct bandgap,²² broad absorbing spectrum in the solar region, high quantum efficiency, and long radiative lifetime.²³ Defects and impurities greatly affect the physical properties of semiconductors and have decisive influences on device performance. Yet, the understanding of the intrinsic defect physics of CsPbI₃ is still limited. For example, what is the dominant intrinsic defect in cubic CsPbI₃? How does the defect determine carrier type and conductivity? Therefore, a comprehensive investigation about intrinsic defects is required.

In this work, we present a systematic density functional theory (DFT) study on the defect physics of CsPbI₃. First, we determine the bandgap of bulk cubic CsPbI₃ (1.02 eV). Second, we reveal that the window for CsPbI₃ growth is narrow and the concentration of Cs is crucial for cubic CsPbI₃ growth. Third, the dominant defect is Pb vacancy, which leads to *p*-type conductivity. Moreover, the high concentration and long lifetime of the *p*-type carrier can be achieved under Pb-poor growth conditions. The direct bandgap nature and lack of recombination center in cubic CsPbI₃ guarantee its good optoelectronic properties.

The first-principles calculations were carried out within the framework of the density functional theory (DFT) using the plane wave pseudopotential method, as implemented in the QUANTUM ESPRESSO software suite.²⁴ The exchange and correlation functional theory was selected as the generalized gradient approximation (GGA)²⁵ with Perdew-Burke-Ernzerhof parameterization.²⁶ Ultra-soft pseudopotentials for Cs, Pb, and I were used. A kinetic energy cutoff of 40 Ry for wavefunctions and $2 \times 2 \times 2$ Monkhorst-Pack K-mesh were used for energy convergence. The convergence threshold on energy was set as 1.0×10^{-10} Ry. The unit cell has five atoms, and their positions were raised within the framework of the cubic space group *Pm3m* structure (Fig. 1). Our calculated lattice parameters of CsPbI₃ are $a = b = c = 6.394 \text{ \AA}$, which are in good agreement with the experimental measurements $a = b = c = 6.289 \text{ \AA}$.²⁷ In advance of the electronic properties and the total energy calculation, the pure crystal structure and the defect-containing supercell structure were optimized so as to obtain the minimum total energy.

^{a)}Author to whom correspondence should be addressed: iamyccheng@njtech.edu.cn

FIG. 1. (a) The unit cell structure of CsPbI₃ with the space group *Pm3m*. (b) 135-atom supercell CsPbI₃ model.

To simulate the formation of point defects in CsPbI₃, the supercell approach was used to calculate the formation energy of a series of intrinsic defects, including vacancies, substitutions, and interstitials in a 135-atom $3 \times 3 \times 3$ supercell. We also check several defects (Cs vacancy, Pb interstitial, and Cs replacing I) in the $4 \times 4 \times 4$ supercell. Compared with defects in the $3 \times 3 \times 3$ supercell, the results are consistent. In addition, the defect states are disperse-less for V_{Pb} , I_{Pb} , and V_{I} shown in Figs. S1 and S2 (supplementary material), which suggests that the $3 \times 3 \times 3$ supercell is large enough for defect calculation. Therefore, we use the $3 \times 3 \times 3$ supercell for all defects. For a defect α that is ionized to the charge state q , the formation energy $\Delta H_f(\alpha, q)$ is a function of both the electron Fermi energy E_F and the chemical potentials of the species involved in the defects^{28–31}

$$\Delta H_f(\alpha, q) = E(\alpha, q) - E(\text{perfect}) + \sum_i n_i \mu_i + q(E_F + E_{\text{VBM}}), \quad (1)$$

where $E(\alpha, q)$ indicates the total energy calculated from the supercell with defect α in the charge state q and $E(\text{perfect})$ is the total energy of the supercell without any defects. n_i is the number of atoms added ($n_i < 0$) or removed ($n_i > 0$) from the supercell. μ_i is the absolute value of the chemical potential of the relevant atom. Herein, in order to express the relationships between the formation energy and the chemical potential of the elemental solids, μ_i is defined as $(\Delta\mu_i + \mu_i^{\text{solid}})$. μ_i^{solid} is the chemical potential of the relevant elemental solid. E_F is the Fermi energy referenced to the E_{VBM} . Therefore, $E_F = 0$ means that the Fermi energy is located at the valence band maximum (VBM). E_{VBM} represents the energy of VBM. The details of calculation could be found in the literature.^{31,32}

As we can see in Eq. (1), the formation energy for different charged defects can be affected by both the Fermi energy induced from electron potential and chemical potential μ_i . Herein, the chemical potential is relevant to the synthetic conditions used in the experiments. First, to prevent formation of elemental solids in the process of synthesis, $\Delta\mu_{\text{Cs}} < 0$, $\Delta\mu_{\text{Pb}} < 0$, and $\Delta\mu_{\text{I}} < 0$ must be satisfied. Second, to prevent the formation of the competing binary compounds, the following constraints also need to be satisfied:

$$4\Delta\mu_{\text{Cs}} + 9\Delta\mu_{\text{Pb}} < \Delta H_f(\text{Cs}_4\text{Pb}_9), \quad (2)$$

$$\Delta\mu_{\text{Cs}} + 3\Delta\mu_{\text{I}} < \Delta H_f(\text{CsI}_3), \quad (3)$$

$$\Delta\mu_{\text{Cs}} + \Delta\mu_{\text{I}} < \Delta H_f(\text{CsI}), \quad (4)$$

$$\Delta\mu_{\text{Cs}} + 4\Delta\mu_{\text{I}} < \Delta H_f(\text{CsI}_4), \quad (5)$$

$$\Delta\mu_{\text{Pb}} + 2\Delta\mu_{\text{I}} < \Delta H_f(\text{PbI}_2), \quad (6)$$

where ΔH_f stands for the calculated formation energy of the corresponding binary compounds. The space group and lattice constants of the related materials are listed in Table S1 (supplementary material). Last, to maintain a stable CsPbI₃ compound, the following equation must be satisfied:

$$\Delta\mu_{\text{Cs}} + \Delta\mu_{\text{Pb}} + 3\Delta\mu_{\text{I}} = \Delta H_f(\text{CsPbI}_3). \quad (7)$$

According to the above mentioned conditions, if the values of $\Delta\mu_{\text{Cs}}$ and $\Delta\mu_{\text{Pb}}$ are determined, then the value of $\Delta\mu_{\text{I}}$ will be limited. Therefore, the chemical potential that stabilizes CsPbI₃ is determined in the purple area surrounded by A, B, C, and D points shown in Fig. 2. From Fig. 2, it is obvious that CsPbI₃ is difficult to grow and the key factor to control the CsPbI₃ growth condition is the concentration of the element Cs. The concentration of element Cs should be limited in a smaller zone due to the narrow window for CsPbI₃

FIG. 2. Chemical potential range for stable CsPbI₃. The lower left part of the figure is the enlarged part of the small rectangle. The purple area among PbI₂, CsI, and CsI₄ is the allowed chemical potential range for CsPbI₃ with the consideration of competing compounds.

FIG. 3. Band structure of CsPbI₃. The left part represents PBE without SOC (the bandgap is 1.44 eV). In the right part, the black lines stand for GGA-PBE (the bandgap is 0.19 eV) and the red lines stand for GW calculations (the bandgap is 1.02 eV).

growth. When the $(\Delta\mu_{\text{Cs}}, \Delta\mu_{\text{Pb}})$ point is on the right-hand side of the C-D line, Cs is too rich in the environment so that CsI or Cs₄Pb₉ will form; when the $(\Delta\mu_{\text{Cs}}, \Delta\mu_{\text{Pb}})$ point is on the left-hand side of the A-B line, Cs is poor so that PbI₂ will form. From the points A-D to B-C, Pb becomes poorer and poorer, and when the $(\Delta\mu_{\text{Cs}}, \Delta\mu_{\text{Pb}})$ point is below the B-C line, the Pb-poor phases CsI or CsI₄ will form.

To explore the formation energy of various defects, the band structure of bulk cubic CsPbI₃ needs to be understood first. From Fig. 3, it is obvious that CsPbI₃ is a direct gap semiconductor with the valence band maximum (VBM) and conduction band minimum (CBM) at the R point in the Brillouin zone. Without the consideration of spin-orbit coupling (SOC), the bandgap is 1.44 eV, which is consistent with the previous computational reports.^{20,33} However, elements Cs, Pb, and I are heavy, and SOC must be considered in calculation. With the conditions of PBE with SOC, the calculated gap is only 0.19 eV, which is consistent with the previous calculated value.³⁴ As we know, the generalized gradient approximated (GGA) will dramatically underestimate the bandgap. To correct the underestimation, we have also performed GW calculations.^{35,36} By using the GW method together with the spin-orbit coupling effect, the calculated bandgap is 1.02 eV, which is the first reported value for bulk cubic CsPbI₃ as far as we know.

For ionized defect, the charged supercell is used and a compensating jellium background is inserted to preserve the overall neutrality. Besides, the electrostatic potential alignment is considered by adding V into the $(E_F + E_{\text{VBM}})$ term, where V is the electrostatic alignment between the doped host and the pure host according to the electrostatic potential of the atomic sites farthest from defects in the core region.^{32,37}

Under the chemical potential condition that maintains the stability of CsPbI₃, we calculated the formation energy of a series of intrinsic point defects, including V_{Cs} (Cs vacancy), V_{Pb} , V_{I} , Cs_i (Cs interstitial), Pb_i , I_i , Cs_i (Cs replacing I, substitution), Cs_{Pb} , I_{Cs} , I_{Pb} , Pb_{Cs} , and Pb_i . Two chemical potential conditions are considered here $(\Delta\mu_{\text{Cs}}, \Delta\mu_{\text{Pb}})$ at A (Pb-rich) and C (Pb-poor) points. Herein, the variation of the formation energy along with the corresponding E_F is depicted in Fig. 4. For a given Fermi energy, only the most stable charge state is plotted. Following Eq. (1), the formation energy of neutral defects does not change with the Fermi energy E_F , while that of ionized acceptor defects (such as V_{Pb}^{2-} and V_{Cs}^{-}) decreases as E_F increases (the slope represents the negative charge q) and that of ionized donor defects (such as V_{I}^{+} and Cs_i^{+}) increases as E_F increases (the slope represents the positive charge state q).

From Fig. 4, we have the following conclusions: (i) Under the Pb-rich (point A) conditions, V_{Pb} has the lowest formation energy among all acceptor defects, and V_{I} has the lowest formation energy among all of the donor defects. Besides, V_{Pb} and V_{I} can achieve a negative value as the Fermi energy changes, which means that they can form spontaneously. Since the formation energies of V_{Pb} and V_{I} are comparable, the formation energy intersection between V_{Pb} and V_{I} can pin the Fermi energy in the middle of the bandgap, 0.6 eV above VBM. Therefore, although the concentrations of both V_{Pb} and V_{I} are very high, the concentration of the carriers is low so that the material is intrinsic with low electronic conductivity under the Pb-rich condition. (ii) Under the Pb-poor (point C) conditions, the formation energies of the donor defects increase, while those of the acceptor defects decrease. It is worth noting that the acceptor

FIG. 4. Calculated defect formation energy as a function of the Fermi energy E_F at the chemical potential points A and C, as shown in Fig. 3. Light (green) and dark (blue) lines represent the donor and acceptor defects, respectively. The most stable donor and acceptor defects are plotted as solid lines. Here, the corrected bandgap of CsPbI₃ is adopted. The vertical line corresponds to the corrected bandgap.

defect V_{Pb} has a lower formation energy than the other donor or acceptor defects. Therefore, the material shows *p*-type conduction with a very high hole concentration. Note that the formation energies of both V_{Cs} and V_I decrease to a negative value as the Fermi energy shifts up to 0.3 eV above the VBM and down to 0.5 eV below the CBM, respectively. Since the carriers produced by the two defects can compensate each other, V_{Cs} and V_I have little influence on the *p*-type conduction.

Above, we discussed whether the defects can form. Next, we discussed whether the defects are responsible for the carrier concentration and how the defects affect the carrier lifetime, which is determined by their transition levels. The defect transition energy level^{29–31} $\varepsilon_x(q/q')$ is defined as the value of the Fermi energy where the formation energy of q equals that of q' of the same defect, i.e.,

$$\varepsilon_x(q/q') = [\Delta E(q) - \Delta E(q')]/(q' - q). \quad (8)$$

When the defects are located at the turning point, namely $\varepsilon_x(q/q')$, in the formation energy plot as shown in Fig. 4, they can change their charge state by releasing or absorbing electrons. Therefore, the material can produce excess carriers to conduct electricity. For example, the turning point of V_{Pb} from the neutral charge state ($q=0$) to the ionized state ($q=-2$) is located at $E_F = -1.35$ eV; thus, its (0/−2) transition energy level is located at 1.35 eV below VBM.

From Fig. 5, the transition energy levels of most of the defects are inside the VBM or the CBM, which means that they are all ionized as long as they form. Therefore, a high concentration of the acceptor defects (such as V_{Cs} and V_{Pb}) will cause a high concentration of hole carriers, which corresponds to the discussions at the point C (Pb-poor). Among all the donor defects, Pb_{Cs} has a deep level at the middle of the bandgap, 0.1 eV below the CBM. Among all the acceptor, I_{Pb} has a deep level at 0.4 eV above the VBM. Under the Pb-rich (point A) conditions, the deep level of Pb_{Cs} can act as the electron-hole trap and recombination center, which reduces the carrier lifetime. Under the Pb-poor (point C) conditions, despite the deep levels of I_{Pb} and Pb_{Cs} , their formation energies are so high that they are hard to form.

FIG. 5. The defect transition levels. The areas under VBM and above CBM are in shaded color. The hollow (solid) points at the levels represent the acceptor defects (the donor defects).

Meanwhile, the disappearance of the recombination center extends the carrier lifetime. Therefore, the Pb-poor is suitable for obtaining excellent *p*-type conductivity. Moreover, the lack of the recombination center in cubic $CsPbI_3$ and direct bandgap indicate its good photoluminescence properties, which have been proved by a lot of experimental works.^{8,13,17,23}

Although the orthorhombic phase of bulk $CsPbI_3$ (indirect bandgap) is thermodynamically stable below 600 K, the cubic phase is stable in nanosize, such as nanocrystals.¹⁷ The bandgap of cubic $CsPbI_3$ is 1.02 eV, which is far below the visual light region (1.65–2.75 eV). Because of the quantum confinement effect, the bandgap for the cubic $CsPbI_3$ nanostructure is increased to the visual light region. The bandgap can be tuned by the size of the nanostructure. Recently, it is discovered that the photophysics of bulk $CsPbI_3$ is better reference when the edge length of the nanostructure is larger than 7 nm.³⁸ Therefore, our present conclusions about the intrinsic defect and carrier type based on bulk cubic $CsPbI_3$ can also be valid for nanostructured $CsPbI_3$ with the size larger than 7 nm.

In conclusion, we have employed the first-principles calculations to study the defect physics of cubic $CsPbI_3$. In order to stabilize $CsPbI_3$, the accurate concentration control of the Cs element is a key factor. By using GW approximation with the spin-orbit coupling effect, the bandgap of $CsPbI_3$ is determined to be 1.02 eV. Under the Pb-rich conditions, V_{Pb} and V_I can pin the Fermi energy in the middle of the bandgap, which results in a low carrier concentration. Pb_{Cs} defect acts as the recombination center to reduce the carrier lifetime. Under the Pb-poor conditions, a high concentration of the acceptor defects V_{Pb} can generate a high concentration of hole carriers and there are no low-energy defects acting as recombination centers. Our results will give guidance for the growth and defect engineering of $CsPbI_3$ for optoelectronic applications.

See [supplementary material](#) for structural details of all related materials in calculations and fat band structures for V_{Pb} , I_{Pb} , and V_I defects.

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